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DEPENDENCE OF HYDROGEN DIFFUSION IN Nb.

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SIMPLE SMALL POLARON MODEL FOR THE HYDROGEN CONCENTRATION
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ABSTRACT

We have generalized simplified small polaron models for the tunneling of interstitials in solids to include interactions between the diffusing particles. This is applied to the calculation of the average hopping rate of hydrogen in Niobium as a function of hydrogen concentration for small concentrations, i.e. for an H/Nb ratio (c) of .06 or less. The hopping of a single H under the influence of nearby, stationary H's was treated. The interactions between interstitials include a hard-core repulsion and a lattice-mediated strain interaction. The tunneling transfer integral was taken to depend on the displacements of nearby Nb atoms. Only tunneling via the ground vibrational level of the interstitials was treated. For $c \leq .06$, the calculated increase in the hopping activation energy as a function of c was linear in c and comparable in magnitude with the experimental increase. Our simplified-model results show that the strain interaction between H's in Nb is important for their diffusion and that this interaction needs to be included in whatever more elaborate diffusion models are developed.

INTRODUCTION

For several years,¹ it has been known that pronounced hydrogen (H) concentration effects exist in the room temperature diffusion of H interstitials in Nb. No detailed theoretical analysis of such effects has yet been made, to our knowledge. However, for the dilute-H case, a recently proposed modified small polaron tunneling model,² appears to be a promising candidate for the diffusion mechanism, and so it would be of interest to generalize this model to include diffusion concentration effects. The

purpose of this paper is to so generalize a simplified version of the proposed model for low concentrations, i.e., $c(\text{H/Nb ratio}) < .06$. Our simplified model includes defect-lattice coupling linear in Nb displacements, and tunneling between the ground vibrational levels of the H. The effects on the motion of a given H due to the strain fields of nearby H's will be included. Both changes in the transfer integral and the difference in initial and final defect energies caused by these strains will be included. Our calculations do not include all the modification of Ref. 2, in particular, no tunneling between the excited vibrational states of the H is included. However, our simplified model can account for a major part of the observed increase in the activation energy with higher H concentrations. Hence, the strain field effects are sufficiently important to require inclusion in whatever more complete models are proposed. This is the main conclusion of this paper.

The increase in activation energy arises in part because the strain interaction between H's is attractive and stronger at close range (causing H-clustering) and in part because the hard cores of nearby H's have a blocking effect on the motion of a given H. In the former effect, due to the clustering and blocking an H must, on the average, move away from a nearby H to a site of higher interaction energy. The blocking raises the effective or average activation energy because the blocking becomes less pronounced at higher temperatures where the clustering is reduced and this behavior is consistent with an average activation energy increase.

An additional effect cancelled part of the above-mentioned increase in activation energy, but did not dominate it. We assumed that the transfer integral between two H-sites is increased by an expansion of the lattice about these sites, i.e., a "non-Condon effect," and that a sufficiently large expansion is necessary before hopping occurs. This has the result that the strain fields of the other H's near the two sites reduce the activation energy. This is so because the nearby H's will, roughly speaking already dilate the lattice near the two sites in question and bring the system closer to the hopping condition to begin with.

II. Nb H_c SYSTEM MODEL AND HOPPING RATE FORMULA

Central to our model for the Nb H_c system is the assumption that, since the H's are lighter and faster than the Nb atoms, they establish quantum vibrational states that adiabatically follow the Nb atomic motions. We further assume, in light of supporting experimental evidence, that the H's vibrate in local modes. The H's tunnel sufficiently seldom that this is a good approximation. Thus, for the situation in between hops, one can treat the Nb lattice quasistatically and define an adiabatic potential energy (APE) for the Nb H_c system in which the Nb

atoms' kinetic energy is neglected but in which the H's are taken to be in their quantum mechanical ground vibrational states. We approximate the adiabatic potential by expanding it in a Taylor series in the Nb displacements and keeping terms linear and quadratic in the displacements. The linear term has the significance of constant, H-induced forces on the Nb atoms while the quadratic term is the lattice harmonic potential energy. We take the latter to be that of the infinite, pure Nb host lattice. We assume the same model for the linear term as Horner and Wagner,³ i.e., each H induces constant, equal longitudinal forces on its Nb second nearest neighbors equal in magnitude to .23 of that of equal, longitudinal forces on the nearest Nb neighbors. The magnitudes are fixed using the observed, macroscopic H-induced volume expansion of the lattice, which is caused by the longitudinal forces. A direct hard-core interaction U_{ij} between H's at sites i and j is assumed that excludes the occupation of up to the third nearest-neighbors of the interstitial lattice. This and the longitudinal force model were used by Horner and Wagner³ to model the α - α' phase transition in Nb H₂. The H-induced forces cause interactions among different H's to arise as the strain field of one H does work against the longitudinal forces induced by another. The energy of interaction, ϵ_{ij} , between two H's at sites i and j , plays a central role in our formalism later on. For values, we will use those calculated by Horner and Wagner,³ using a Born von Karman model for the Nb lattice, but we will average those involving the same i - j separation to obtain ϵ_{ij} dependent only on the separation. For two H's lying zero through twelve n.n. shells apart, we use the following averaged values (the zeroth shell corresponds to the self energy) -4174, -2907, -1967, -1218, -589, -426, -212, 86, 97, 500, 314, -110, and -16.

To describe the tunneling process, the occurrence probability approximation of Holstein⁴ is used in which the lattice is treated classically and quasistatically. Within this approximation, an H vibrates rapidly in a well of the quasistatically moving lattice until a thermal fluctuation induces a quasistatic lattice distortion such that the system's total adiabatic energy would be unchanged if the H were moved to the vacant final site. For each such "coincidence event," the H has a certain probability of tunneling to the potential final site. The adiabatic potential energy increase involved in this lattice distortion constitutes the activation energy (AE) appropriate to the given H-configuration and the given lattice distortion. If a hard core is blocking the hop, the AE is infinite and the hop doesn't occur. In the simplest polaron models, the average AE, i.e., the result after the rate is averaged over all possible coincidence events, is equal to the lowest possible coincidence-event AE. In our model, we take not the coincidence event, of lowest energy, but we assume that a dilation in addition to that of the lowest-lying coincidence event is necessary to sufficiently increase the transfer integral to make a hop possible. This additional dilation, lattice activa-

ion, or higher-lying coincidence event requires an additional adiabatic potential energy increase beyond that of the lowest possible, which means a larger average activation energy.

We will average over all dilations beyond a certain higher-lying threshold dilation, which we now describe. It will involve equal dilations about the initial and final H-sites, the dilation about each site having equal n.n. Nb and equal second n.n. Nb longitudinal displacements in the same proportion as the forces of the ϵ_{ij} . This plausible assumption allows the ϵ_{ij} to be used in the formalism to also describe the dilation. The overall magnitude of the dilation necessary is determined from the dilute-H case by taking the additional activation energy of lattice activation to be the experimental dilute-H AE (106 meV for $T > 290K$) minus the calculated minimum AE, e_0 , which equals $-(\epsilon_{JJ} - \epsilon_{KK})/4$ for a hop between sites J and K. When other nearby, static H's are present, they will cause the extra dilation needed for the hop of a given H to be partially present initially before any thermal fluctuations. We assume that the transfer integral is sufficiently large during a coincidence event that the probability of a hop during a coincidence event is unity. This is the so-called adiabatic hopping regime.⁴ We also assume that all memory of previous hops is lost before another occurs.

We now briefly describe how our hopping rate formula is derived and then write it. We first found the hopping rate for a given initial H-configuration and given higher-lying coincidence event and then integrated the result over all higher-lying events followed by an average over initial H-configurations. The rate for a given event has a prefactor, ω , independent of c , but with a T^{-2} dependence. This can be established by working through the coincidence event formalism in Appendix II of Ref. 4, with W_c set to 1 (adiabatic hopping) and with the additional dilation condition added. The AE of the given higher-lying event is obtained by setting the prehop and posthop APE's equal to obtain one condition and then by minimizing the prehop APE subject to this and the condition that the extra dilation be a certain amount. After making use of the approximation $\text{erfc}(x) \approx (x\pi^2)^{-1/2} \exp(-x^2)$ in the integration (which we numerically showed to be valid in our case) we obtain for $W^{JK}(\{n_g^a\})$, the rate for an interstitial n.n. hop from site J to site K with initial H-configuration $\{n_g^a\}$:

$$W^{JK}(\{n_g^a\}) = \omega \exp\{-[(E^b - E^a)/4e_0]^2 / (e_0 kT) + B^2/kT\} / B$$

where E^b and E^a are the pre- and posthop APE's respectively, and B is $(\Delta e_b^2 + 2\epsilon_{JJ}^2 + 2\epsilon_{KK}^2 + 4\epsilon_{JK}^2)n_g^a / [4\epsilon_{JJ}^2 + 4\epsilon_{KK}^2 + 8\epsilon_{JK}^2]$. Δe_b is the additional AE in the dilute-H case necessary for the additional transfer-integral-increasing dilation and the rest of B involves the static strains that initially provide part of the additional dilation. $E^b - E^a$ can be written $-2\epsilon_{JJ}(U_{JJ} - U_{KK} + U_{JJ} - U_{KK})n_g^a$. The form of the exponent

above clearly shows that the initial strains modify the lowest-lying-event activation energy through $E^b - E^a$.

The rate W^{JK} should be averaged over the initial H-configurations. We approximate the probability of occurrence of a given H-configuration as $\prod_{\ell} P_{J\ell}^{\ell}(n_{\ell}^a)$, i.e., $P_{J\ell}^{\ell}(1)$ and $P_{J\ell}^{\ell}(0)$, the prehop probabilities of a static H being or not being at site ℓ depend only on the H (about to hop) at site J. We set $P_{J\ell}^{\ell}(1)$ to $(c/6) \exp(-Y_{J\ell}/kT)/D$ and $P_{J\ell}^{\ell}(0)$ to $(1-c/6)/D$, where $Y_{J\ell} = \epsilon_{J\ell} + U_{J\ell}$ and $P_{J\ell}^{\ell}(1) + P_{J\ell}^{\ell}(0)$ equals 1. We made the additional approximation in the exponent of W^{JK} of keeping only terms linear in the n_{ℓ}^a . Similarly, we expanded the denominator in a Taylor series and kept only linear-in- n_{ℓ}^a terms. In our numerical calculations, we estimated the above approximations to be good for $c \leq .06$, when 1% or less of the available interstitial sites are occupied. We also estimated the error in W^{JK} due to using ϵ_{ij} values for only twelve n.n. shells (setting the rest to zero) to be 10%. To do this the twelve ϵ_{ij} values were extrapolated to larger distances using a modified Debye model for the phonons.

We consider only the c -dependent part of the hopping rate, Z_p , defined by $\ln Z_p = \ln \langle W^{JK} \rangle - \ln(w') + (e_0 + \Delta e_h)/kT$. We fitted our calculated $\ln Z_p$ as a function of T by least squares to the formula $\ln f + \Delta E/kT$, where ΔE is a c -dependent change in the effective or average ΔE and f is a multiplicative factor describing how the effective prefactor changes with c . The calculated $\ln Z_p$ fitted this form fairly well over the limited T range involved in both the calculation and in the data of Fig. 1, i.e. 400-600K. Had we not subtracted the T^{-2} -dependent w' out of $\ln Z_p$, it would have dropped out anyway. ΔE and f are plotted in Fig. 1.

DISCUSSIONS AND CONCLUSIONS

Fig. 1 shows that our hopping model predicts an increase in the activation energy with c , as observed experimentally. For $c \leq .06$, where our approximations are valid, the increases in activation energy ΔE , predicted by our model is roughly comparable with the experimental increase. The linear extrapolation of the calculated ΔE to higher c , yields ΔE values also roughly comparable to the experimental ones. We conclude that, the effect of the H-H strain interaction on the diffusion rate is sufficiently strong that it needs to be included in any more realistic model for the H-concentration effect on H diffusion in Na.

For $c < .06$, our calculated prefactor multipliers f were not incompatible with the experimentally determined f . However, the linear extrapolation to higher c of the calculated f did not fit the data at all. These discrepancies could be due to the crude assumptions made concerning the transfer integral dependence on lattice displacements, i.e., the sudden turn-on for the threshold

coincidence event, and the assumption that adiabatic hopping obtained during a coincidence event.

REFERENCES

1. H. C. Bauer, J. Völkl, J. Tretkowski, and G. Alefeld, Z. Physik B29, 17 (1978).
2. D. Emin, M. I. Baskes, and W. D. Wilson, Phys. Rev. Lett. 42, 791 (1979).
3. H. Horner and H. Wagner, J. Phys. C 7, 3305 (1974).
4. T. Holstein, Ann. Phys. (NY) 8, 343 (1959).

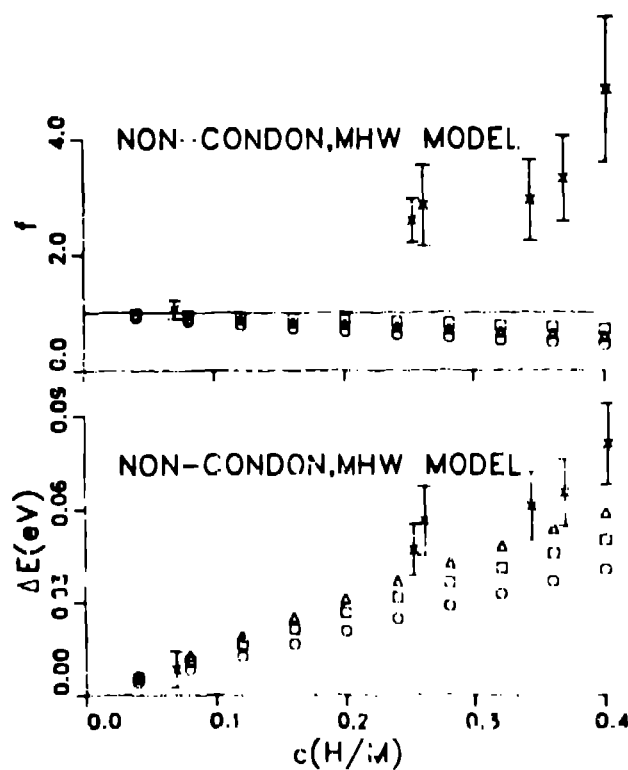


Fig. 1. The X's and error bars give experimental values for ΔE , and for f . The squares, circles, and triangles give our calculated values for an interstitial n.n. hop, a 2nd n.n. hop, and a 3rd n.n. hop, respectively. The latter two are not discussed in the text. MHW indicates that our averaged $\langle J \rangle$ values were used.